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Araştırma Makalesi

Metallurgical Slags from Converter Furnace - Specificity of Their Phase and Chemical Composition

Döner Fırından Metalurjik Curuflar - Faz ve Kimyasal Bileşimlerinin Belirliliği

Iwona Jonczy[1]*

[1]*Silesian University of Technology, Faculty of Mining and Geology, Institute of Applied Geology, Gliwice, POLAND*
**Responsible Author: iwona.jonczy@polsl.pl*

Abstract
Metallurgical slags, which come into being as a secondary product of steel making, are more and more often used in different economy fields. In Poland there is a search for solutions to close down dumping grounds of metallurgical wastes and to manage the slags which come into being during the current production to avoid their long-term storage. This work must be preceded by multidirectional research, among which analyses of phase and chemical compositions of slags play an important role. In the mineral composition of the slags, apart from crystalline components, the presence of glaze and iron metallic precipitations was noticed. The degree of crystallization of individual components was different depending on the speed of cooling an alloy, which also allowed us to distinguish their different microstructures. Chemical composition of the metallurgical slags is variable and depends on: the type of the used charge material, fluxes, refining additives and a used melt technology. Nevertheless in all tested slags iron was presented in the largest quantities.

Key words: Metallurgical slag, metals, phase composition.

Özet
Çelik üretiminde ikincil ürün olarak elde edilen metalurjik cüruflar farklı alanlarda ekonomik olarak çok daha fazla sıklıkla kullanılmaktadır. Polonya'da metalurjik cürufların zemine dökülerek kapanmasına çözüm bulabilmek ve uzun dönem depolanmalarından kaçınılması için mevcut üretim sürecinde oluşan cürufların düzenlenmesi için araştırmalar yapılmaktadır. Bu çalışma cürufların kimyasal bileşimleri ve fazlarının analizi arasında önemli bir rol oynayan çok yönlü bir araştırma ile ilerlemelidir. Cürufların mineral bilişimlerinde kristal bileşimlerinden ayrı olarak camlaşmanın ve demir metalik çökelmenin varlığına dikkat edilmiştir. Bileşenlerin ayrı ayrı kristalleşme dereceleri farklı mikro yapılarının aynı zamanda ayrılmasında izin veren soğuma hızına bağlı olarak farklılık göstermiştir. Metalurjik cürufların kimyasal bileşimi değişkendir ve kullanılan şarj malzemesinin tipine, eritkenlere, rafine katkılarına ve kullanılan eriyik teknolojisine bağlıdır. Bulunla birlikte, test edilen bütün cüruflarda, demir büyük miktarlarda bulunmuştur.

Anahtar kelimeler: *Metalurjik cüruf, metaller, faz bileşimi.*

1. Introduction
Upper Silesia is one of the best industrialized regions in Poland (south part of Poland). The beginnings of mining and smelting have been dated here on the Middle Ages. Beside coal mining, iron and steel industry has become one of the most developed industries in this region. But on the other hand iron and steel industry became especially problematic, because of considerable amounts of wastes - mainly metallurgical slags, coming into being during production.

In the past slags were gathered on the dumps. Presently, in view of widely accepted pro-ecological policy, attention has been drawn to the possibility of using metallurgical slags, both the slag collected on dumps and the slags generated by ongoing production processes, as a secondary material. Technical researches of slags have shown that they may be used to produce aggregates for highway engineering. There are also numerous researches carried out in order to acquire metals from metallurgical slags. All these activities must be preceded by multidirectional laboratory analyses connected, among others, with learning the chemical and phase composition of slags (Cioroi et al. 2010; Jonczy 2007, 2011; Jonczy et al. 2012; Mateus et al. 2011; Rai et al. 2002). Moreover the study of slag are already carried out at the stage of their forming inside of the blast furnace (Kudrin 2007; Kozhukhov 2013). Based on the detailed studies, connections of metals with slag phases and possibilities of their migration from slags during their utilization, could be determined.

In this article there is presented a characterization of a chemical and mineralogical composition of metallurgical slags from one steel works in Poland. The research was carried out on 4 types of slag originating as a secondary product in a converter furnace during 4 different cycles of smelting. The differences between successive cycles are connected with variable conditions of cooling a slag alloy and with a slightly different character of a furnace charge which is connected first of all with a various amounts and different type of scrap added to the charge. Slags analyzed macroscopically are similar to one another, they are characterized by black color and they are brittle and porous.

2. Research methods
Chemical composition of slags was determined in the Activation Laboratories Ltd. – ACTLABS in Canada using the TD-MS and TD-ICP methods. Spectral analysis in microareas was carried out at the Institute of Non-ferrous Metals at Gliwice (Poland) and the X-ray analysis – at the Institute of Ceramics and Building Materials – department also at Gliwice. The research with the application of scanning microscopy was carried out at the Scanning Microscopy Laboratory of Biological and Geological Sciences of the Department of Biology and Earth Sciences of the Jagiellonian University in Kraków (Laboratory at the Institute of Geological Sciences). Microscopic observations in transmitted light were made at the Institute of Applied Geology of the Faculty of Mining and Geology of the Silesian University of Technology in Gliwice (Poland).

3. Results
Metallurgical slags could contain a considerable amount of metals, so it is very important to control their concentration, especially when we use slags as a secondary material.

In the chemical composition of the analyzed metallurgical slags there dominate Fe (14,14-20,00%), in the second place is Mn whose concentration in all samples is similar - ~1% (tab. 1). Ni, Ti and Pb appear in changeable amounts and their increased concentration was noticed in the sample No 2. In the sample No 3 the content of Cr increases, whereas in the sample No

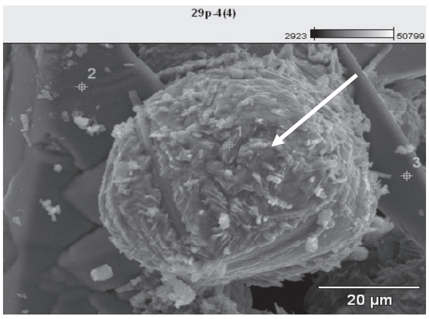
4 the content of Cu, V and Zn. Variation of elements is connected with additives used in the metallurgical process (Cr, Mn, Ni, Ti, V) and the type of scrap added to the furnace charge (Cu, Pb, Zn). However, in general, all these differences of metals concentration are not too large.

Element		Slag No 1	Slag No 2	Slag No 3	Slag No 4
Fe	[Mass%]	20,00	17,90	14,14	17,60
Mn	[Mass%]	1,06	1,00	1,00	1,08
Ti	[Mass%]	0,060	0,729	0,208	0,230
As	[ppm]	1,0	0,9	2,9	4,0
Cd	[ppm]	0,01	0,20	0,10	0,20
Cr	[ppm]	666	1280	1580	834
Co	[ppm]	0,9	1,0	0,8	0,7
Cu	[ppm]	11,5	16,0	22,2	23,4
Ni	[ppm]	9,8	14,6	11,1	9,9
Pb	[ppm]	3,2	10,3	6,1	5,1
V	[ppm]	652	632	679	728
Zn	[ppm]	12,2	7,5	7,5	26,5

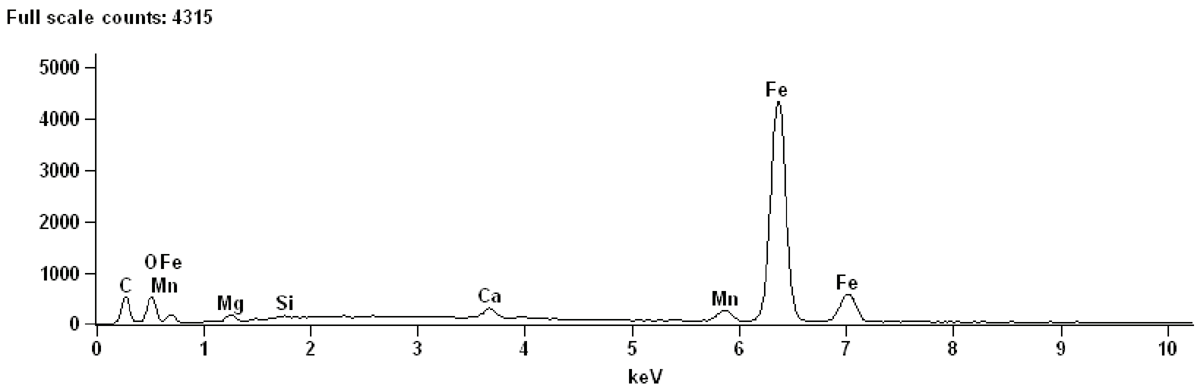
Table 1. Concentration of metals in metallurgical slag from converter furnace.
Tablo 1. *Dönüştürücü fırından metalurjik cüruflarda metallerin konsantrasyonu.*

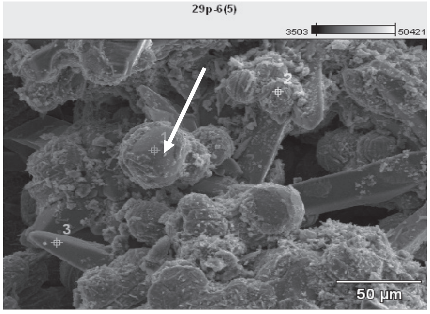
Iron, which is present in the largest quantities in the chemical composition of all studied slags, occurs in different forms. The largest group of iron phases are iron oxides. The following phases were distinguished among them: wustite FeO, magnetite Fe_3O_4 and hematite Fe_2O_3:

- Wustite creates globular forms. This type of wustite is formed through the oxidation of iron and by assuming by this phase morphological forms characteristic for the liberation of metals. Wustite often contains an admixture of calcium, magnesium and manganese oxides (Figure 1).



Oxide [Mass%]				
FeO	**MnO**	**MgO**	**CaO**	**SiO_2**
92,69	**3,38**	**2,14**	**1,39**	**0,40**





Oxide [Mass%]							[Mass%]
FeO	CaO	Cr_2O_3	Al_2O_3	SiO_2	MnO	MgO	Cl
57,60	38,31	1,47	0,97	0,66	0,51	0,36	0,10

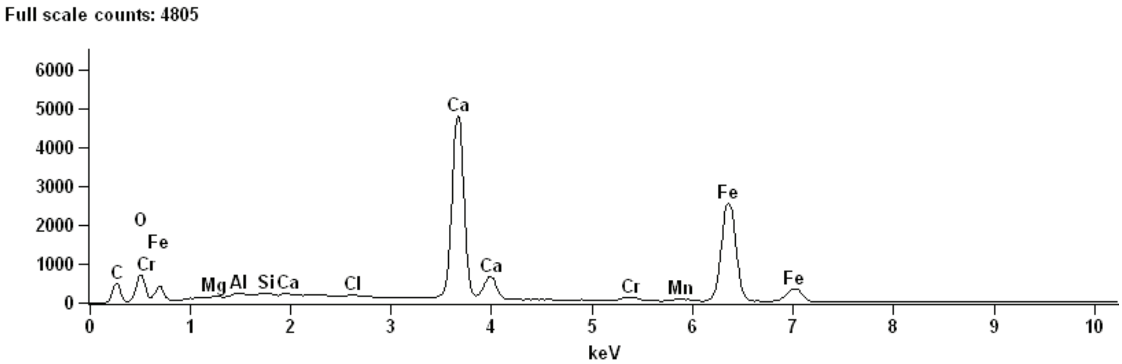


Figure 1. Globular forms of wustite; Scanning Microscopy: SEM and EDS spectrums with chemical analyses.
Şekil 1. *Vustitin küresel şekilleri; Tarama Mikroskopu: kimyasal analizleri ile SEM ve EDS görüntüleri.*

● Magnetite only sometimes forms large crystals which have crystallized directly from the alloy, characterized by the habits of squares. Usually it forms fine, non-transparent grains which cover surface of the other phase components or are accumulated in the cracks of the glaze or forms an inclusions in the silica phases (Figure 2).

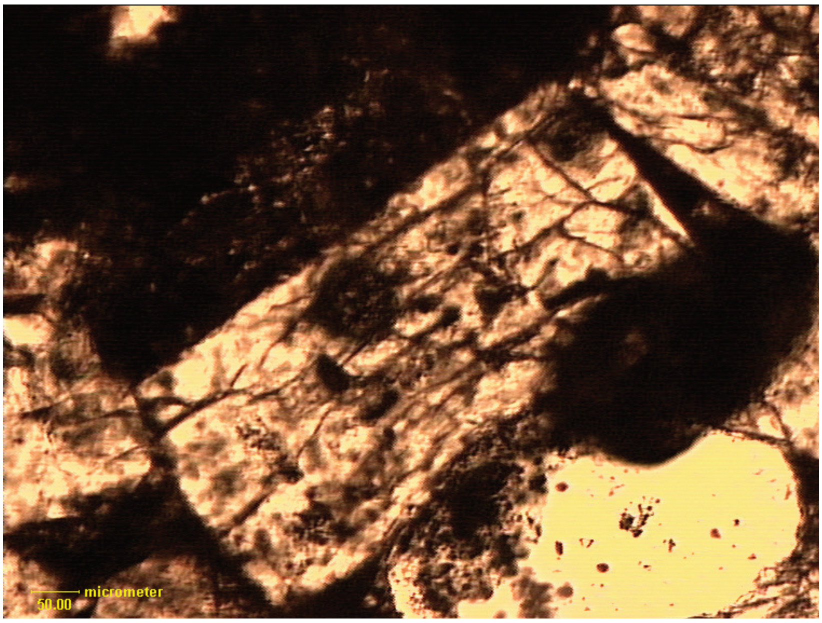


Figure 2. Crystal of melilite with inclusions of magnetite; transmitted light, magnification 100x, one nicol.
Şekil 2. *Magnetitin kalıntıları ile melilit kristalleri, ışık iletilmiştir, büyütme 100x, bir nikol.*

● Hematite can form very fine grains dispersed among other phase components to larger, sharp-edged crystals (Figure 3). Fine grains are called pigment, which gives the glaze red colouring. For larger grains red colour is also characteristic.

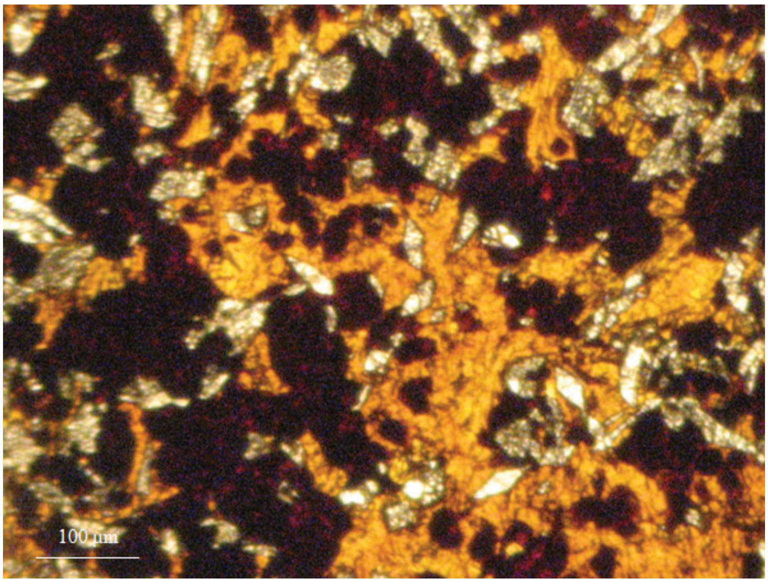


Figure 3. Crystals of hematite; transmitted light, magnification 100x, one nicol.
Şekil 3. *Hematit kristalleri; ışık iletilmiştir, büyütme 100x, bir nikol.*

In some kinds of slags after steel production we can also find solid solution of FeO-MnO-MgO, which is characterized by skeleton forms (Figure 4), but in the studied slags this solution was observed in very small amounts.

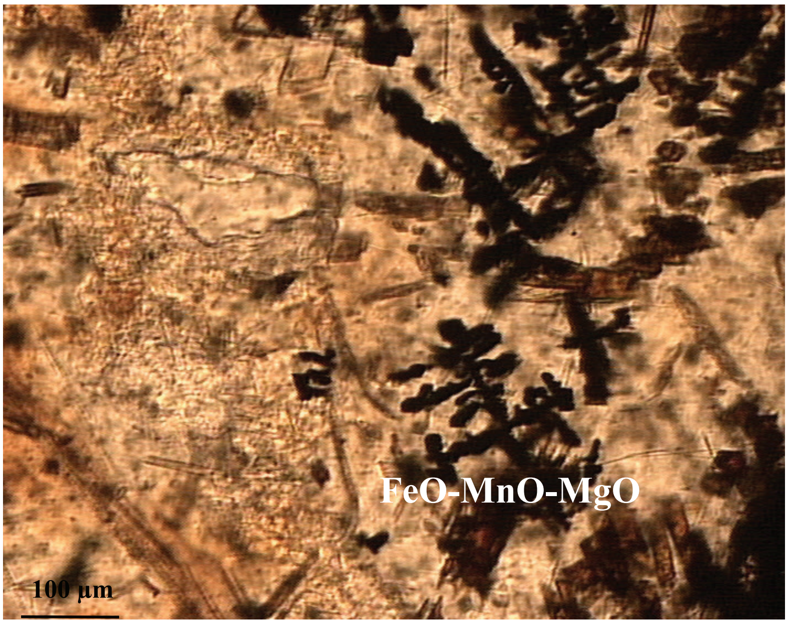
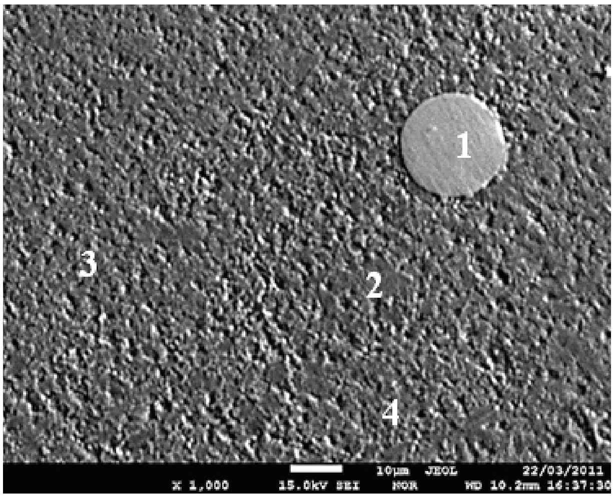


Figure 4. Skeleton forms of solid solution of FeO-MnO-MgO, transmitted light, magnification 100x, one nicol.
Şekil 4. *FeO-MnO-MgO'nun katı çözümünün çatı formları, ışık iletilmiştir, büyütme 100x, bir nikol.*

Iron also:
- occurs as fine drops not separated during metallurgical process (point 1, image 5);
- is dispersed in glaze (images 5-8).

On based observations in microareas, the detailed phase composition of slags was presented (Figures 5-8) as also diversification of slags microstructure, which is a result of phases crystallization in variable conditions of cooling a slag alloy.

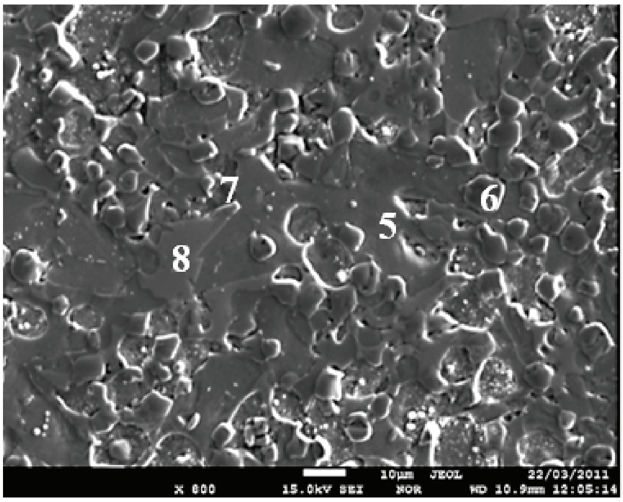


Point	Element [Mass%]									
	O	Si	Al	Fe	Mn	Ca	S	Zn	Pb	Σ
1	0,28	0,03	0,01	99,09	0,06	0,42	0,01	0,01	0,09	100,00

Point	Oxide [Mass%]											Σ
	SiO_2	TiO_2	Al_2O_3	Cr_2O_3	V_2O_5	FeO	MnO	MgO	CaO	P_2O_5	ZnO	PbO	
2	3,02	0,10	0,10	0,34	-	59,11	5,16	15,81	16,00	0,32	0,05	-	100,01
3	21,11	0,16	0,20	0,37	0,07	12,37	1,56	15,10	46,45	2,53	0,06	0,02	100,00
4	26,74	0,24	0,54	0,06	0,09	6,67	0,54	1,16	60,95	2,94	0,07	-	100,00

Figure 5. Microphotography and chemical analysis of the slag No 1

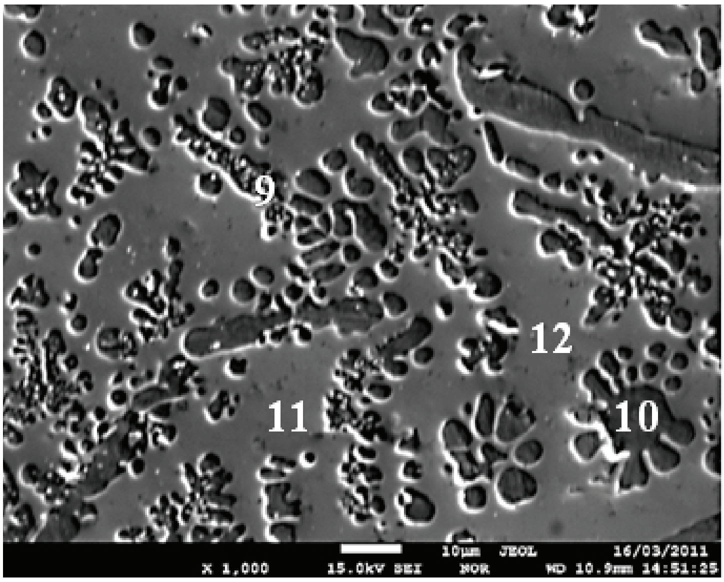
Şekil 5. *Cüruf No 1'in kimyasal analizi ve mikro fotoğrafı.*



Point	Oxide [Mass%]												Σ
	SiO_2	TiO_2	Al_2O_3	Cr_2O_3	V_2O_5	FeO	MnO	MgO	CaO	P_2O_5	ZnO	PbO	NiO	
5	23,26	-	0,41	0,01	-	3,50	0,41	0,47	69,28	1,58	0,01	-	0,03	100,00
6	-	-	-	0,15	0,04	13,29	1,33	83,05	2,05	-	-	0,01	-	100,00
7	9,30	0,05	42,72	0,02	-	2,92	0,21	0,26	38,96	2,30	0,29	0,43	0,06	100,01
8	1,71	1,33	7,18	0,12	0,51	40,76	0,35	0,56	46,98	0,29	0,13	0,03	-	100,00

Figure 6. Microphotography and chemical analysis of the slag No 2.

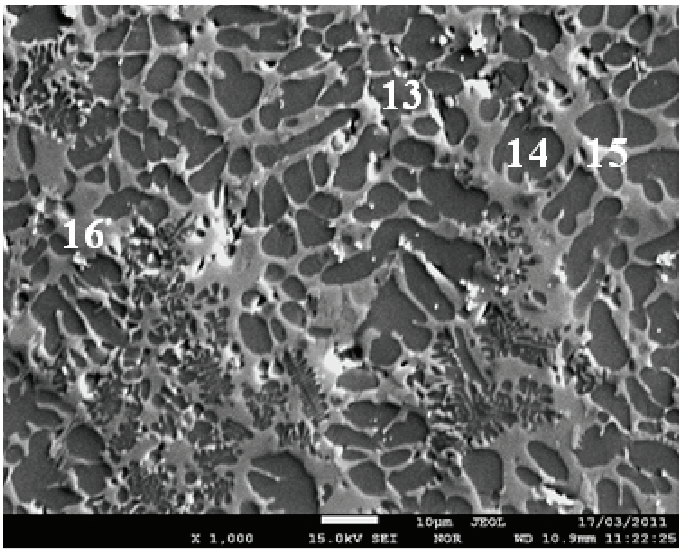
Şekil 6. *Cüruf No 2'nin kimyasal analizi ve mikro fotoğrafı.*



Point	Oxide [Mass%]												Σ
	SiO_2	TiO_2	Al_2O_3	Cr_2O_3	V_2O_5	FeO	MnO	MgO	CaO	P_2O_5	SO_3	ZnO	
9	22,06	0,24	0,54	0,13	-	5,89	1,35	18,54	48,52	2,60	2,60	0,07	100,00
10	30,59	0,11	0,30	-	0,04	1,33	0,11	0,43	64,09	2,93	2,93	0,05	100,00
11	5,14	1,03	1,64	0,36	0,06	35,52	6,91	1,71	47,10	0,43	0,43	-	100,00
12	5,21	0,10	2,18	0,06	0,06	37,29	4,95	3,40	46,06	0,45	0,45	0,05	99,99

Figure 7. Microphotography and chemical analysis of the slag No 3.

***Şekil** 7. Cüruf No 3'ün kimyasal analizi ve mikro fotoğrafı.*



Point	Oxide [Mass%]													Σ
	SiO_2	TiO_2	Al_2O_3	Cr_2O_3	V_2O_5	FeO	MnO	MgO	CaO	P_2O_5	SO_3	ZnO	PbO	
13	29,73	0,19	0,31	0,01	0,11	1,64	0,13	0,08	64,22	3,52	0,03	0,03	-	100,00
14	30,05	-	0,27	0,04	0,09	1,58	0,10	0,18	64,06	3,58	-	0,04	-	99,99
15	0,12	-	-	0,03	-	64,42	10,20	10,82	14,25	-	-	0,11	0,06	100,01
16	3,20	1,78	2,24	0,59	0,10	41,16	2,70	1,01	46,74	0,44	-	0,04	-	100,00

Figure 8. Microphotography and chemical analysis of the slag No 4.

***Şekil 8.** Cüruf No 4'ün kimyasal analizi ve mikro fotoğrafı.*

In the slag No 1 there appear great amounts of glaze with only single metal drops. Drops of metals are represented by almost pure iron (point 1, image 5), glaze of this slag (points 3, 4, image 5) contains big amounts of CaO, SiO_2, FeO, MgO and smaller amounts of other oxides. In the glaze there are demixing zones with variable chemism (point 2, image 5).

Sporadically, in the slag No 1 there are observed crystal nuclei, their bigger amounts are noticed in the slag No 2, where the presence of crystallites is a proof of interrupted crystallization of phase components as a result of sudden cooling of an alloy. Then the cooling process must have proceeded gradually with a slower decrease of temperature, which is proved by demixing zones. In the slag No 2, beside the glaze (point 5, image 6), the following components were distinguished: periclase (point 6, image 6), calcium aluminates (point 7, image 6) and ferrites (point 8, image 6).

The slags No 3 and No 4 were submitted to slower cooling, which allows us to observe the dendrite and skeleton structure. These slags, in contrast to the slags No 1 and 2, contain small amounts of glaze in comparison to crystalline phases On the images 7 and 8 the significant growth of silicate phases – dicalcium silicates and calcium-magnesium silicates (dark gray dendrites) against the background of glaze (light gray boxes) was shown. The glaze from the slags No 3 and 4 in comparison to the glazes from the slags No 1 and 2 contains smaller amounts of SiO_2. Its main components are CaO and FeO with an additive of MnO and MgO (points 11, 12, image 7; points 15, 16, image 8). The silicate phase dendrites are merged into glaze, which is a proof of their earlier crystallization, which then was interrupted as a result of cooling an alloy. The remaining components congealed in the form of glaze.

Dicalcium silicates are one of the most popular silica component of the slags from the converter furnace, on base scanning microscopy ten kinds of them were distinguish. Their formulas are presented below:
1. $(Ca_{1,92-1,98}Mg_{0,01-0,02})[Si_{1,00-1,03}O_4]$,
2. $(Ca_{1,92}Mg_{0,02})[(Si_{1,01}Al_{0,03})O_4]$,
3. $(Ca_{1,96}Mg_{0,03}Ti_{0,02})[(Si_{0,95}Al_{0,04})O_4]$,
4. $(Ca_{1,94}Mg_{0,02}Na_{0,006})[(Si_{0,96}Al_{0,07})O_4]$,
5. $(Ca_{1,96}Fe_{0,02-0,04})[(Si_{0,84-0,85}P_{0,12-0,13})O_4]$,
6. $(Ca_{1,96-2,06}Fe_{0,03-0,08})[(Si_{0,79-0,83}P_{0,10-0,14}Al_{0,008-0,03})O_4]$,
7. $(Ca_{2,00}Fe_{0,03}Ti_{0,01})[(Si_{0,83}P_{0,10}Al_{0,0007})O_4]$,
8. $(Ca_{1,52-1,53}Mg_{0,46-0,47}Mn_{0,01-0,02})[Si_{0,99-1,00}O_4]$,
9. $(Ca_{1,76}Mg_{0,43}Mn_{0,06}Ti_{0,03})[(Si_{0,81}Al_{0,03})O_4]$,
10. $(Ca_{1,97-1,98}Fe_{0,03-0,04}V_{0,004-0,006})[(Si_{0,80-0,83}P_{0,11-0,12}Al_{0,02-0,04})O_4]$.

A X-ray analysis was carried out in order to make a detailed description of phase components, which would allow us to give a specific name of a given phase. That research has proved the presence of all the mentioned components in slags and shown the presence of phases whose identification with microscopic methods was hindered. On base X-ray analysis, among crystallite of the studied slags the following phases were distinguished: solid solution of brownmillerite-srebrodolskite $Ca_2(Al,Fe)_2O_5$-$Ca_2Fe_2O_5$, alite $Ca_3[O|SiO_4]$, calcium olivine α-$Ca_2[SiO_4]$, mayenite $Ca_{12}Al_{14}O_{33}$, jadeite $NaAl[Si_2O_6]$ and solid solution of melilites (gehlenite-akermanite) $Ca_2Al[(Si,Al)_2O_7]$-$Ca_2Mg[Si_2O_7]$.

Some of these phases, like melilites (image 2), were also observed during microscopic studies but only occasionally big, well-crystallized silicate phases were found. In a slag alloy the crystallization process is suddenly stopped during cooling and this is a reason that the majority of slags components congeals in the form of glaze. Some of them occur in the form of small crystalline nuclei, whereas well-developed crystals which can be identified during microscopic observations are rare and the glaze is dominant among slags components.

4. Conclusions

Mineralogical and chemical analyses of slags which came into being during a direct production of a converter furnace showed that their chemical composition changed in accordance with additives applied in the steel process and the type of scrap added to the furnace charge.

The phase composition of slags was also changeable as well as the form of development of individual phases. Glaze dominated in slags subjected to sudden cooling, crystallization of silicate phases was noticed where the temperature of an alloy did not drop too violently.

In all kinds of analyzed slags the same composition of elements was noticed, but their contents were variable. The highest concentration of metals was connected with iron. Iron may occur in metallurgical slags as fine drops not separated from slag during a metallurgical process, may form polymetallic aggregates, inclusions and its own phases (especially oxide ones), iron can also be hidden in the structure of silicate phases. A considerable amount of iron and the other metals are dispersed in glaze and amorphous substance.

Numerous possibilities of slags application determine the need to learn the material in the best possible way, especially in relation to the phase composition as well as the chemical composition. Knowing these aspects makes it possible to draw conclusions, among others, about possibilities of release of heavy metals from slags components and their migration to the environment. This knowledge will be useful in making economic activities connected with using metallurgical slag as a secondary material. Utilization, which will economically cost effective and ecologically safe for the environment.

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